

# **Two-Photon Absorption Measurements: Establishing Reference Standards.**

## **REPORT**

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### **Principal Investigator:**

Dr. Marek Samoc

e-mail address: [marek.samoc@anu.edu.au](mailto:marek.samoc@anu.edu.au)

Institution: Laser Physics Centre, The Australian National University

Mailing address: Canberra, ACT 0200, Australia

Phone: +61 2 6125-4611

FAX: +61 2 6125-0029

### **Co-investigators:**

Dr. Anna Samoc

e-mail address: [anna.samoc@anu.edu.au](mailto:anna.samoc@anu.edu.au)

Laser Physics Centre, The Australian National University

Canberra, ACT 0200, Australia

Dr. Paul A. Fleitz

e-mail address: [Paul.Fleitz@wpafb.af.mil](mailto:Paul.Fleitz@wpafb.af.mil)

Materials and Manufacturing Directorate, Air Force Research Laboratory,

WPAFB, OH 45433-7702, USA

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## **1. INTRODUCTION**

Two-Photon Absorption (TPA) is an important phenomenon taking place at high light intensities and consisting in simultaneous absorption of two low energy photons to generate a higher energy excited state of a material. Materials showing efficient two-photon absorption are required for a number of applications including information storage, photonic signal processing, optical power limiting, nonlinear microscopy of biological systems etc. In the simple case of a material containing a concentration  $N$  (in  $\text{cm}^{-3}$ ) of two-photon absorbing molecules, under steady-state conditions, the absorption can be quantified through the equation:

$$\frac{d\Phi}{dz} = -N\sigma\Phi - N\sigma_2\Phi^2$$

where  $\Phi$  is the photon flux (in photons/( $\text{cm}^2\text{s}$ )),  $\sigma$  is the one-photon absorption cross section (in  $\text{cm}^2$ ) and  $\sigma_2$  is the two-photon absorption cross section (in units of  $\text{cm}^4\text{s}$ ). The unit for the TPA cross section is often given as  $\text{cm}^4\text{s}/(\text{photon molecule})$ , and, for practical reasons,  $10^{-50} \text{ cm}^4\text{s}$  has been adopted as a unit of the cross section called a Goeppert-Mayer ( $1\text{GM} = 10^{-50} \text{ cm}^4\text{s}$ ).  $\sigma_2$  is the key photophysical parameter describing the nonlinear absorption, however, despite a considerable effort of many teams to determine reliable values of the cross sections of TPA molecules, there are still many discrepancies between the results obtained by different groups, using different techniques and under different experimental conditions (the laser parameters like pulse duration, repetition rate, peak light intensity; the sample parameters like concentration of the two-photon species, type of matrix, eg the solvent used, geometry of the sample, eg relation of its thickness to the Rayleigh range of the beam used)<sup>1</sup>. This report contributes to the knowledge of parameters influencing the two-photon cross section values obtained by direct absorption measurements and provides representative data for comparison with other techniques.

## **2. EXPERIMENTAL TECHNIQUE**

### **Open and closed aperture Z-scan with a tunable amplified femtosecond laser system**

These measurements were performed using a laser system consisting of a Clark-MXR CPA-2010 Ti-sapphire regenerative amplifier and Light Conversion TOPAS optical parametric amplifier.

The typical methodology for the determination of cubic nonlinearity of dyes is performing Z-scan measurements in solutions in common solvents (chloroform, THF,  $\text{CH}_2\text{Cl}_2$ ), in 1 mm or 2 mm glass cells. The wavelength range, which can be used is

500-2000 nm, the pulse duration is about 150 fs, the repetition rate of the pulses is 80-250 Hz, the pulse energy is typically about 1  $\mu$ J/pulse. The spot size parameter  $w_0$  is typically 30-60  $\mu$ m,  $\Delta\phi = 0.5 - 1.5$  rad for a cell+solution. This corresponds to light intensities on the order of 50 - 150 GW/cm<sup>2</sup>.

All nonlinearities are calibrated against silica, for which the nonlinear refractive index is assumed to be  $n_2=3\times 10^{-16}$  cm<sup>2</sup>/W independent of the wavelength<sup>2</sup>.

Z-scans are fitted using the equations derived by Sheikh-Bahae et al <sup>3</sup>, the concentration dependences of the real and imaginary parts of the nonlinearity are used to calculate the solute complex hyperpolarizability  $\gamma^4$ . The imaginary part of the hyperpolarizability can be related to the two-photon absorption cross section. It should be noted that the hyperpolarizability is a molecular property and in principle should not depend on the solvent, unless the interactions with the solvent modify the molecule. On the other hand, the two-photon cross section can also depend on the solvent through the presence of local field corrections depending on the refractive index of the solvent.

Errors in the measurements are generally much higher for the real part of  $\gamma$  compared with the imaginary part of  $\gamma$ , due to the fact that the refractive nonlinearity is measured as an increment to that of the  $n_2$  of the solvent and the cell whereas the absorptive nonlinearities of the cell and the solvent are negligible.

### **3. RESULTS**

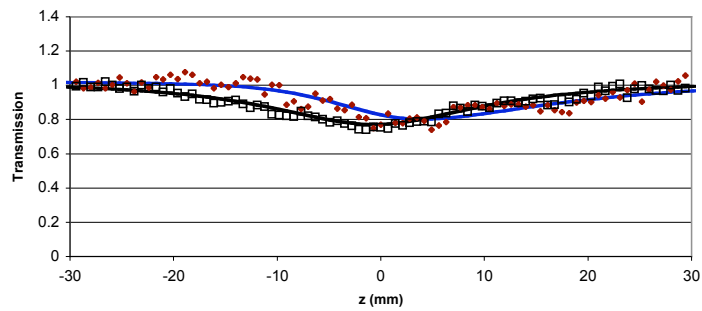
#### **3.1 bis-MSB**

*p*-Bis(*o*-methylstyryl)-benzene (abbreviated bis-MSB) is a well-known laser dye which has been selected as one of the standards for investigations of two-photon absorption cross sections by the method of two-photon induced fluorescence. We have investigated the two-photon absorption of this dye through direct measurement of nonlinear absorption, in order to compare the results obtained by different techniques and in different laboratories.

The measurements were performed in chloroform solutions at several concentrations of the solute (0% to about 1.5% by weight) and the results were analyzed by numerical fitting of the Z-scan curves. Some data were also obtained for THF solutions. A peak value of  $\sigma_2 \approx 40$  GM (1 GM =  $10^{-50}$  cm<sup>4</sup>s) was found at 630 nm for bis-MSB with the light intensities of about 100 GW/cm<sup>2</sup>. At this intensity three-photon absorption is also seen at longer wavelengths. The real part of complex hyperpolarizability  $\gamma$  was determined as well. Below we show examples of Z-scans

obtained for 1.4 wt% bis-MSB in chloroform.

a)



b)

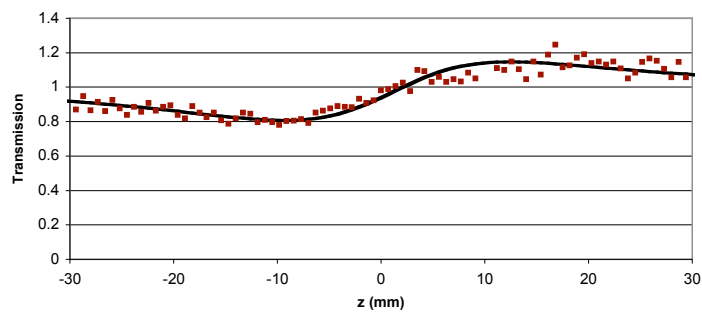
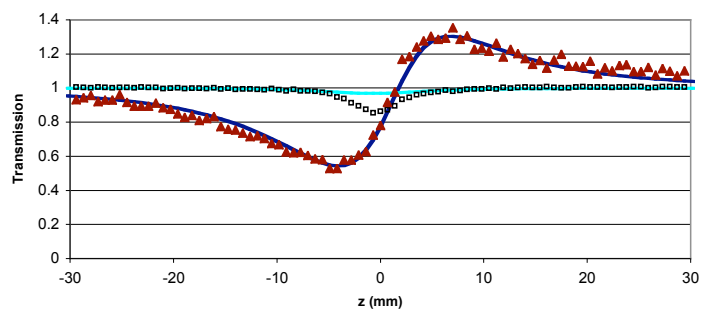


Figure 1a: Closed-aperture (diamonds) and open-aperture (squares) Z-scans for bis-MSB in chloroform at 660 nm. Figure 1b: The closed-aperture scan for the solvent. Full lines are theoretical fits.

At 660 nm the two-photon absorption dominates both open-aperture and closed-aperture transients with negative refractive nonlinearity of the solute dominating over the positive contribution of the solvent.

a)



b)

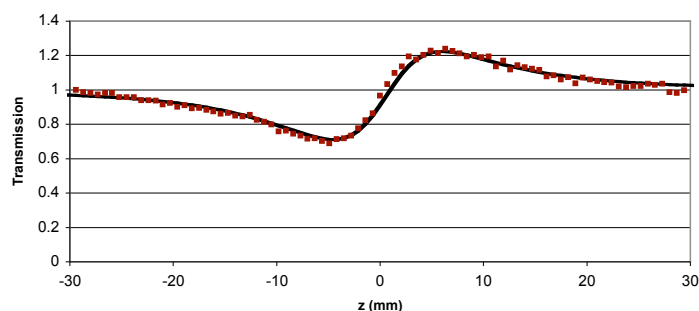


Figure 2 Closed-aperture (triangles) and open-aperture (open squares) Z-scans for bis-MSB in chloroform at 780 nm (a) compared with the scan for the solvent (b). Full lines are theoretical fits.

The two-photon absorption at 780 nm is already very weak but higher-order losses are visible in the open-aperture scan. The closed-aperture scan shows clearly a positive refractive contribution from bis-MSB at this wavelength.

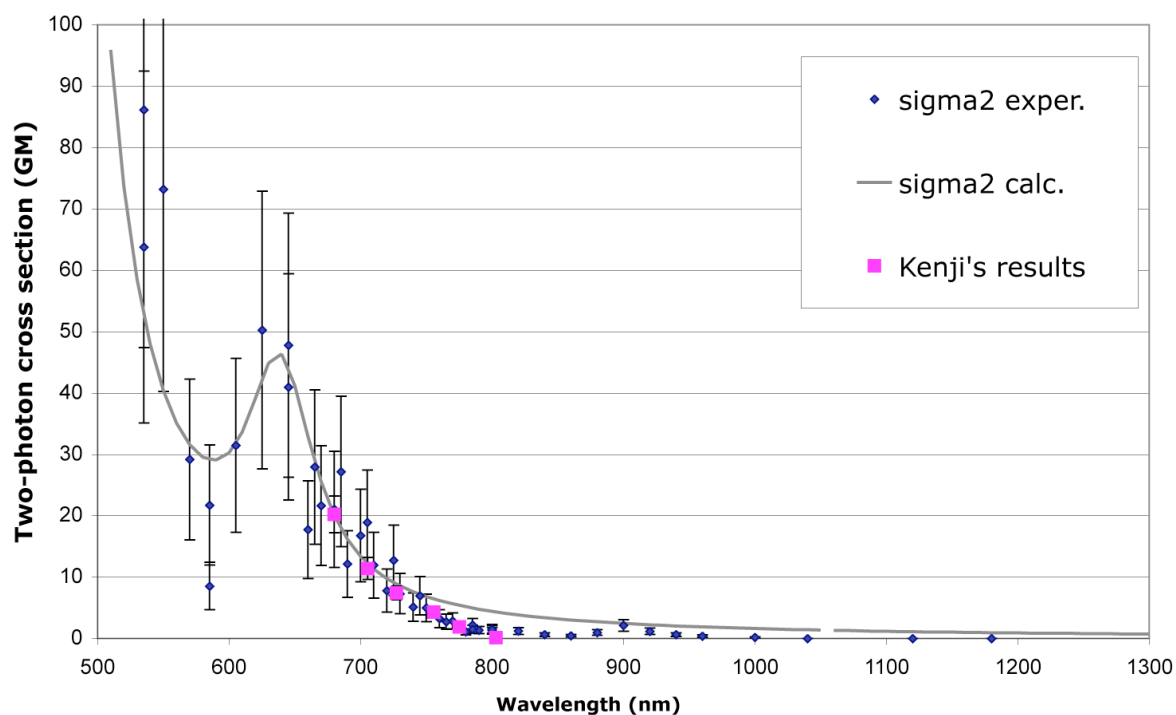


Figure 3 Two-photon absorption cross-section of bis-MSB compared with results from Dr. Kenji Kamada.

The imaginary part of  $\gamma_{\text{im}}$  and the two-photon absorption cross section results obtained for bis-MSB can be reasonably well fitted with a simple dispersion formula:

$$\gamma(-\nu; \nu, -\nu, \nu) = \left[ \frac{A}{(\nu_a - 2\nu - i\Gamma_1)} + \frac{B}{(\nu_b - 2\nu - i\Gamma_2)} \right] \times \frac{1}{[\nu_a - \nu - i\Gamma_1]^2}$$

where  $\nu_a = 31250 \text{ cm}^{-1}$  ( $\lambda = 320 \text{ nm}$ ),  $\nu_b = 45454 \text{ cm}^{-1}$  ( $\lambda = 220 \text{ nm}$ ),  $\Gamma_1 = \Gamma_2 = 1500 \text{ cm}^{-1}$ . However, these parameters do not provide a good fit for the real part of the hyperpolarizability  $\gamma_{\text{real}}$  shown in Figure 4. The origin of this discrepancy is unclear, but contributions of additional multiphoton mechanisms (e.g. excited state absorption) are likely.

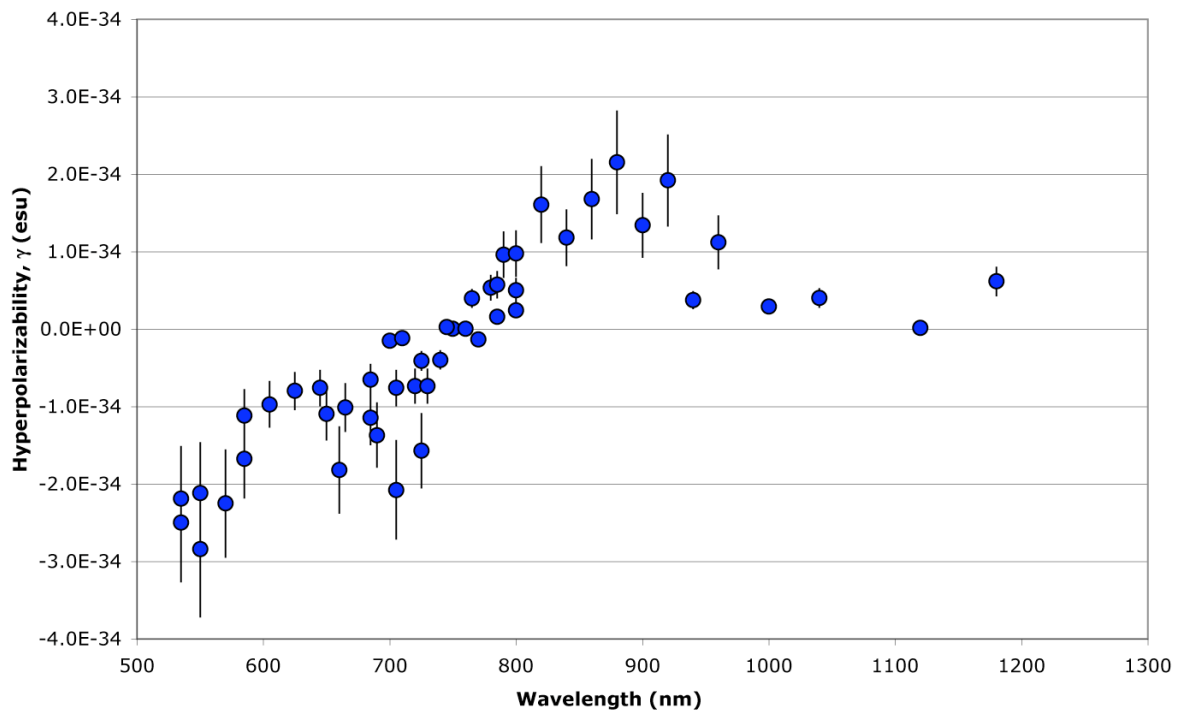
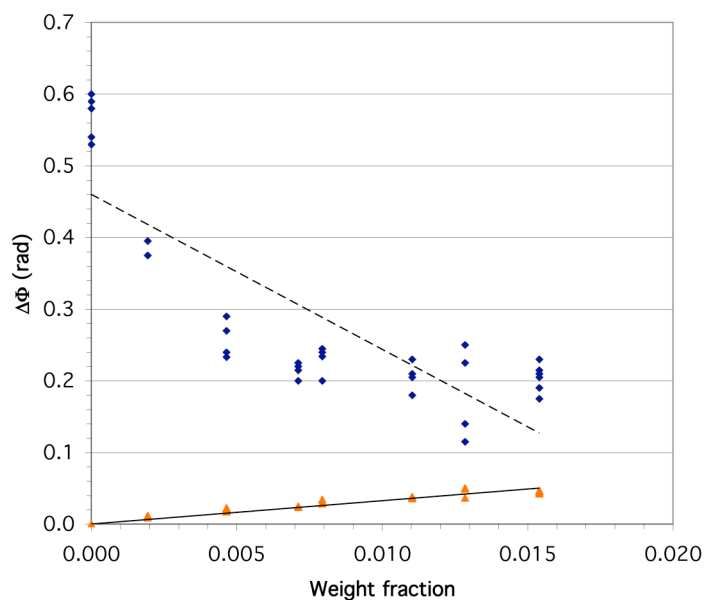


Figure 4 The real part of the hyperpolarizability of bis-MSB obtained from measurements on chloroform solutions. For comparison,  $|\gamma| = 1.3 \times 10^{-34} \text{ esu}$  was evaluated for bis-MSBM from DFWM measurements at 800 nm<sup>5</sup>.

However, it is also of importance that the real part of the hyperpolarizability may depend on the solvent used for the experiments. Figure 5 shows comparison of concentration dependences of the real and imaginary part of the nonlinear phase shift  $\Delta\Phi$  for solutions of bis-MSB in chloroform and in THF. It appears that while the slope of the dependence for the real part of  $\Delta\Phi$  and the real part of  $\gamma$  are negative for the  $\text{CHCl}_3$  solution, they are positive for the THF solution. In addition, the

dependence of the real part of phase shift on the concentration of bis-MSB in chloroform solution appears to be not linear. Similar effects were also reported by us previously for phenylenevinylene oligomers<sup>1</sup>.

a)



b)

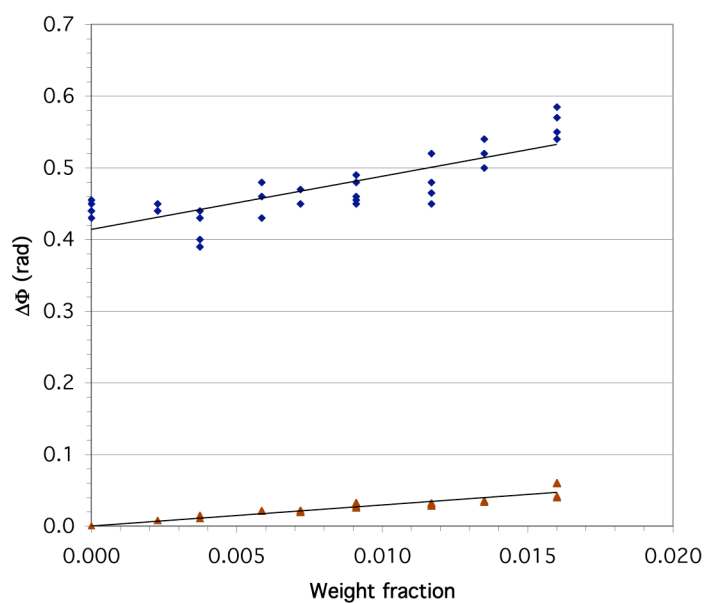


Figure 5 Comparison of the concentration dependences of the real (diamonds) and imaginary (triangles) part of the nonlinear phase shift for bis-MSB in chloroform (a) and in THF (b) solutions.

### 3.2 AF-350

The dye known as AF-350 is a strong two-photon absorber. We have investigated properties of a solution of AF-350 in dichloromethane at a concentration



of  $\sim 1\%$ . Fig. 6 shows the results of the determination of the real and imaginary part of the hyperpolarizability as well as the imaginary (absorptive) part of the nonlinearity presented as the two-photon absorption cross section.

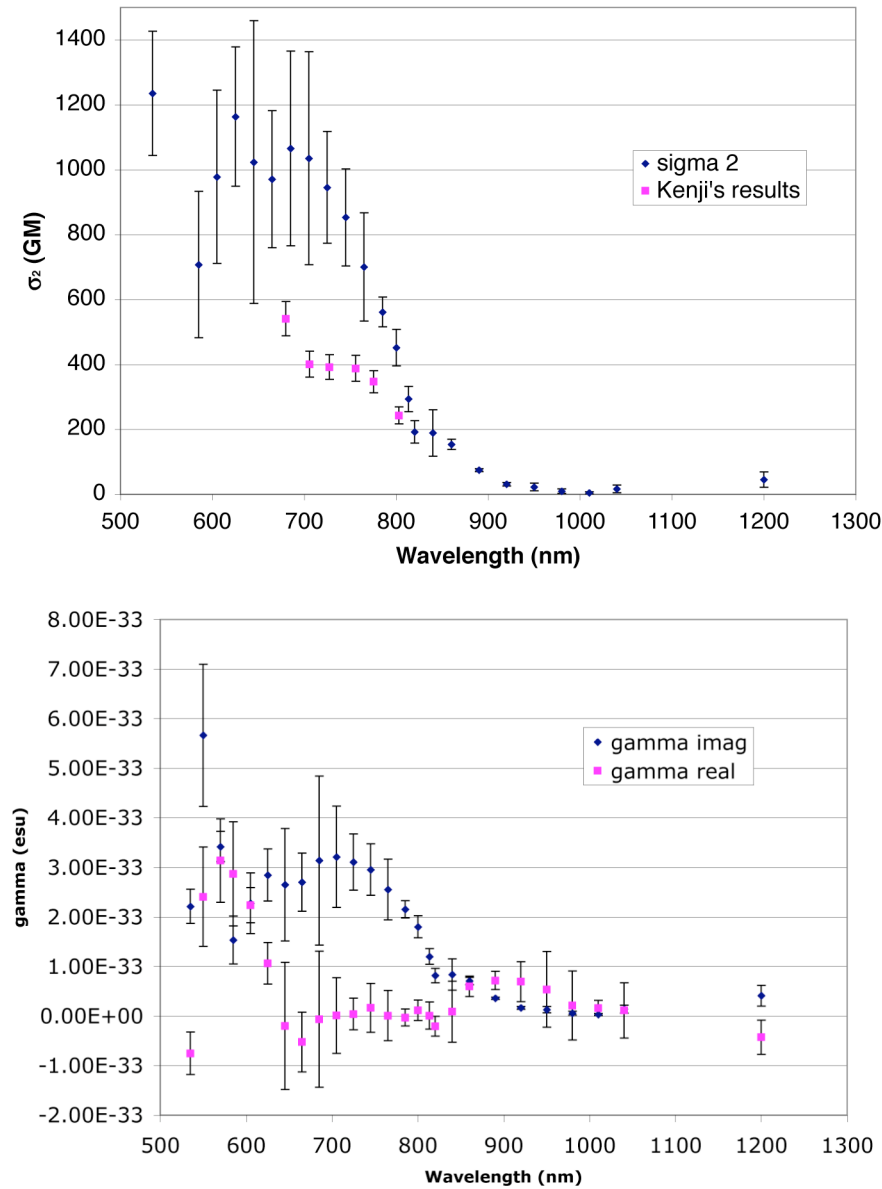


Figure 6 Two-photon cross sections and real and imaginary parts of the hyperpolarizability  $\gamma$  for AF-350.

The results obtained for AF-350 cannot be treated as precise because of the fact that some coloration of the sample was seen in the area exposed to the laser beam: an indication of some photochemical changes. It is likely that the photochemical changes may be contributing to overestimation of the two-photon cross section.

### 3.3 Coumarin 503

Coumarin 503 (also known as Coumarin 307) was studied by measurements performed on solutions in two different solvents: chloroform and tetrahydrofuran (THF). The results obtained on the two solutions indicate that Coumarin 503 has relatively low values of the two-photon cross section and the spectrum is basically centred around 750 nm. Data obtained for chloroform solutions (6.36 wt%) are lower than those for THF (1 wt%). However, the difference may also arise from different concentrations used for the two experiments.

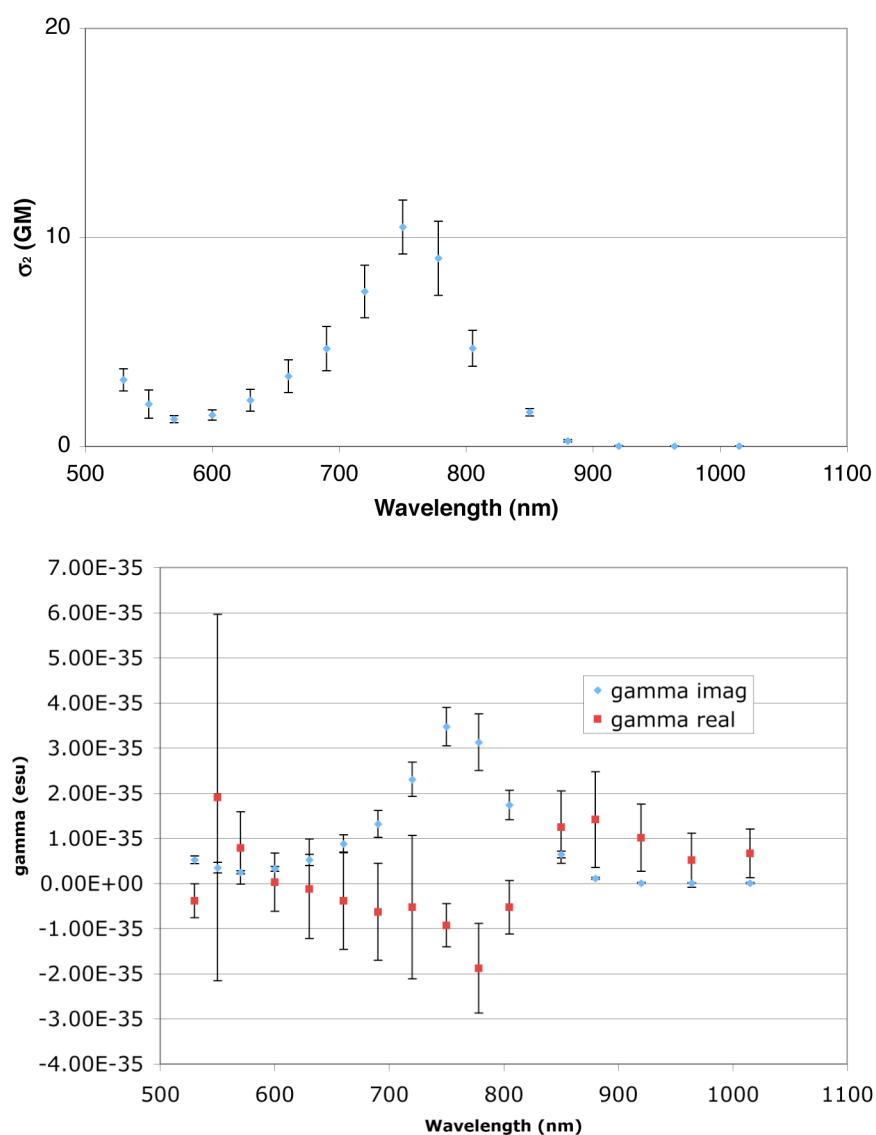


Figure 7 Two-photon cross sections (missing units) and real and imaginary parts of the hyperpolarizability  $\gamma$  for Coumarin 5030 obtained from measurements in a 6.36% chloroform solution.

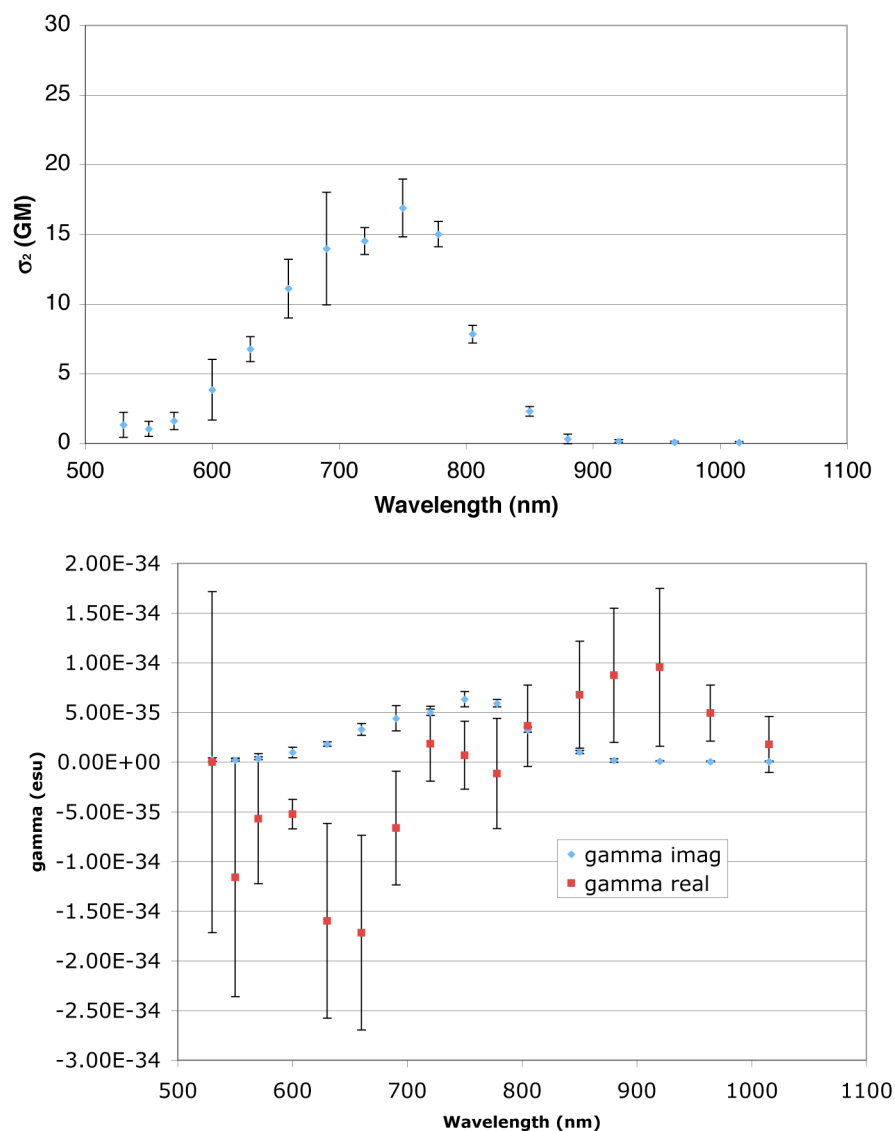


Figure 8 Two-photon cross sections and real and imaginary parts of the hyperpolarizability  $\gamma$  for Coumarin 503 obtained from measurements in a 1% THF solution.

### 3.4 Rhodamine B

Rhodamine B was investigated in two forms: as chloride and as perchlorate. In both cases the solvent was ethyl alcohol. The results are presented below. One should note the change of sign of the nonlinear absorption cross section at short wavelengths. This is a typical behavior of many dyes at the onset of one-photon absorption.

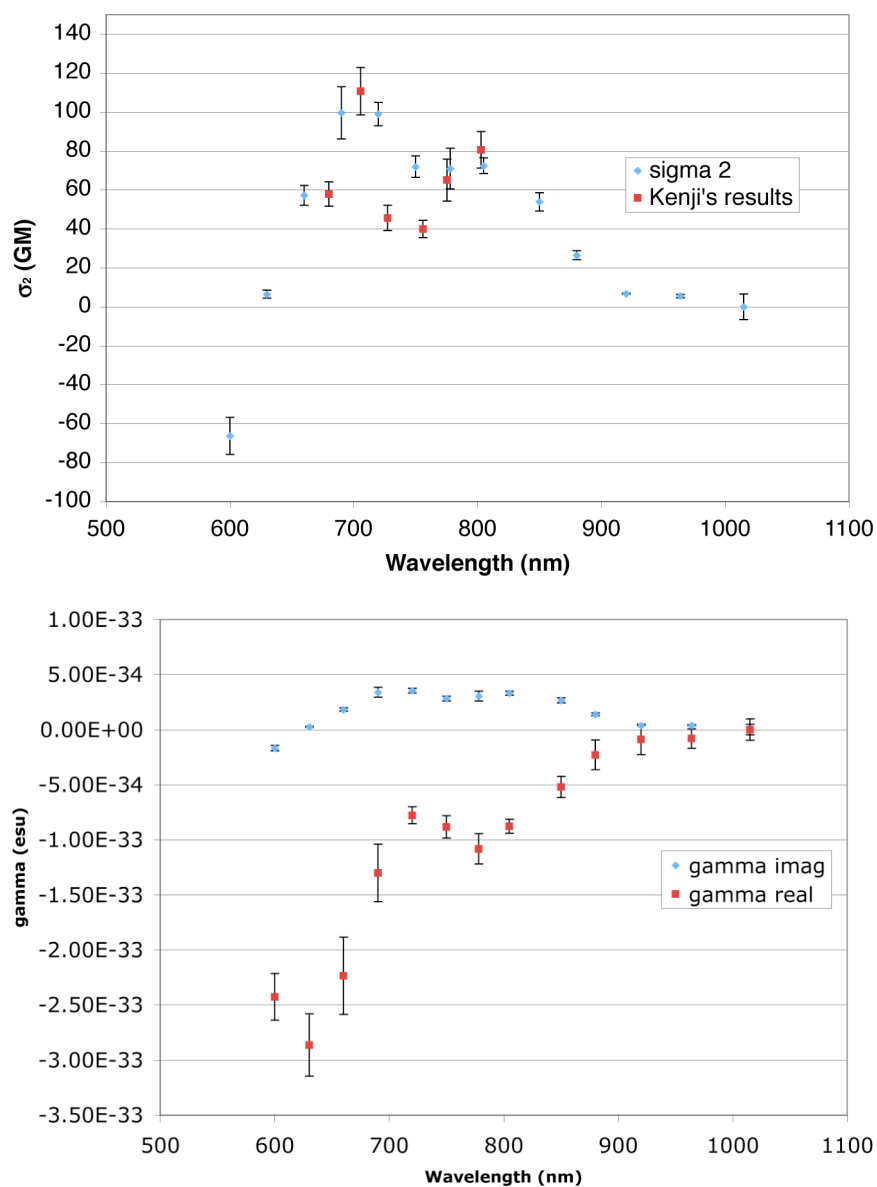


Figure 9 Two-photon cross sections and real and imaginary parts of the hyperpolarizability  $\gamma$  for Rhodamine B chloride obtained from measurements in 1.047% Ethanol solution.

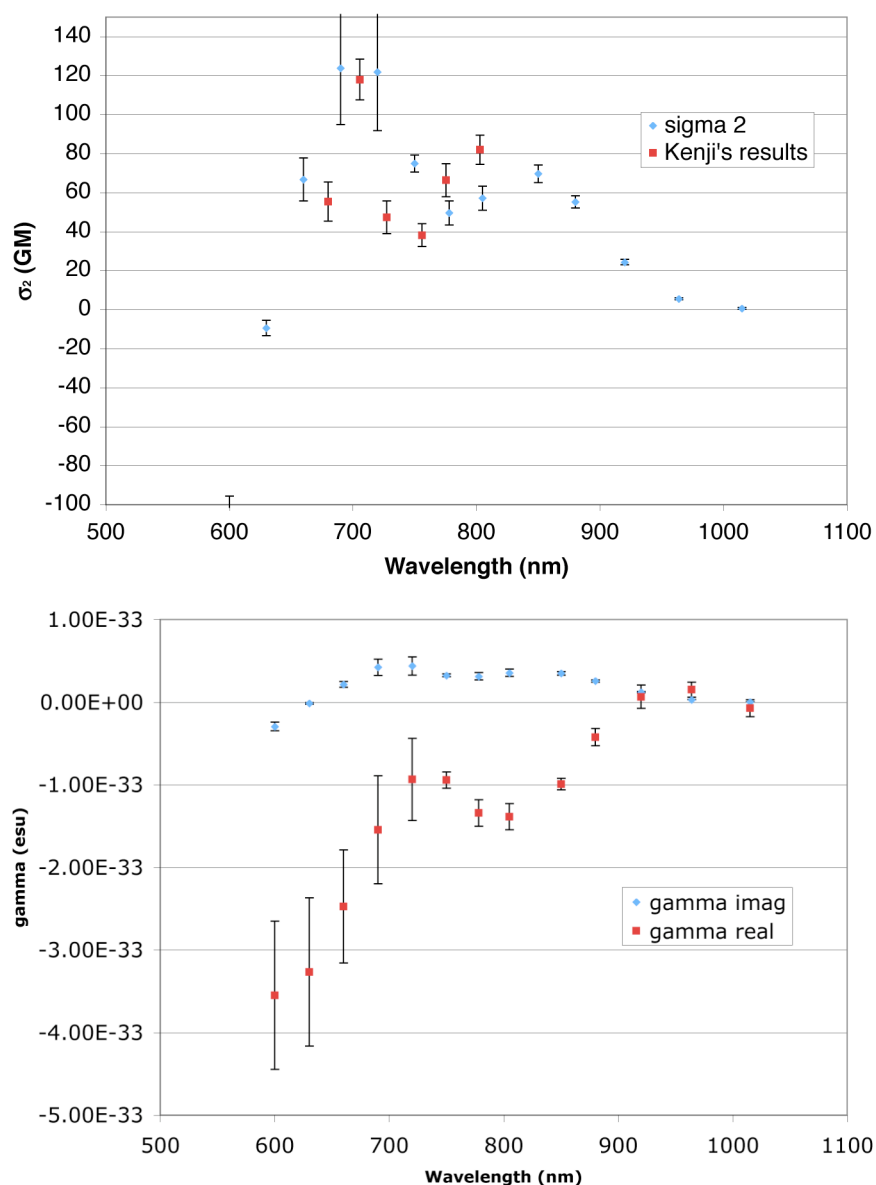


Figure 10 Two-photon cross sections and real and imaginary parts of the hyperpolarizability  $\gamma$  for Rhodamine B perchlorate obtained from measurements in 1.038% Ethanol solution.

### 3.5 MPPBT

MPPBT<sup>6</sup> was suggested by Dr. Kenji Kamada as a possible standard for two-photon absorption measurements. The results obtained on a DMSO solution of MPPBT are presented below. One notes that the high values of the two-photon cross section reported by Kamada et al<sup>6</sup> due to the resonance with the one-photon absorption band are well reproduced here.

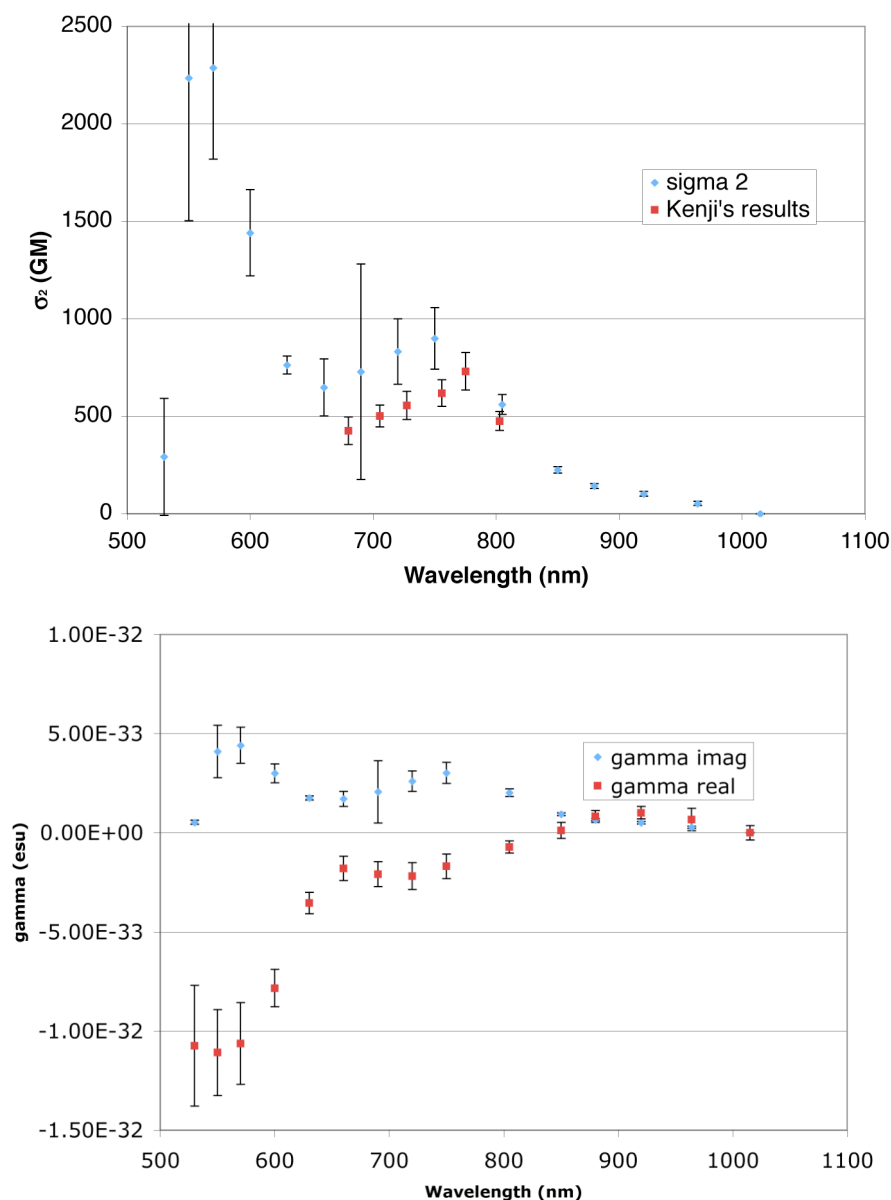


Figure 11 Two-photon cross sections and real and imaginary parts of the hyperpolarizability  $\gamma$  for MPBBT obtained from measurements in 0.452% DMSO solution.

### 3.6 Fluorescein

Since fluorescein was suggested as one of the possible standards, attempts were made to determine its two-photon cross section in several different solvents: THF, ethanol, chloroform and a pH=11  $\text{K}_2\text{CO}_3$ -water solution. Unfortunately, the solubility in chloroform was too small, and the two-photon absorption in THF and

ethanol was negligible. The only results which are reliable are those for the pH=11 solution. They are presented below.

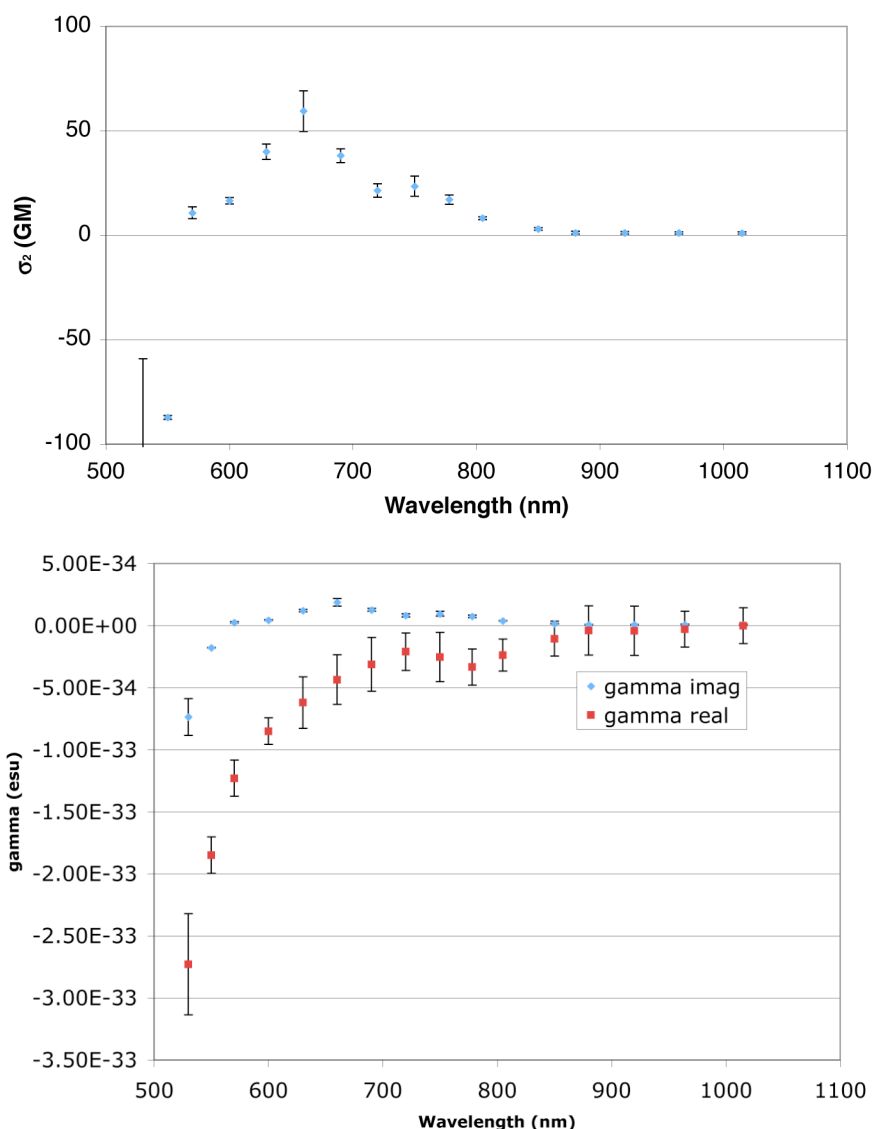


Figure 12 Two-photon cross sections and real and imaginary parts of the hyperpolarizability  $\gamma$  for fluoresceine obtained from measurements in 0.55% pH=11 water solution (made with potassium carbonate).

#### 4. DISCUSSION

The raw results presented here will now be the basis of discussions with other members of the group coordinated by Dr. Paul Fleitz and conclusions will be drawn concerning the reliability of the determination of the two-photon absorption cross sections and the suitability of various standards and measurement techniques.

Joint publications should follow.

It is interesting to compare the results obtained here with those of the well-known paper of Xu and Webb<sup>7</sup>. Figures 13-15 show overlap of the results with those from that paper. Results for bis-MSB are not shown: the data of Xu and Webb are much lower than those shown here. Relatively good agreement is seen for Coumarin 307 and Rhodamine B (although the present data are lower in magnitude and do not show the long wavelength peak), and no agreement at all is seen for fluorescein. Most likely, Xu and Webb used another form of that dye.

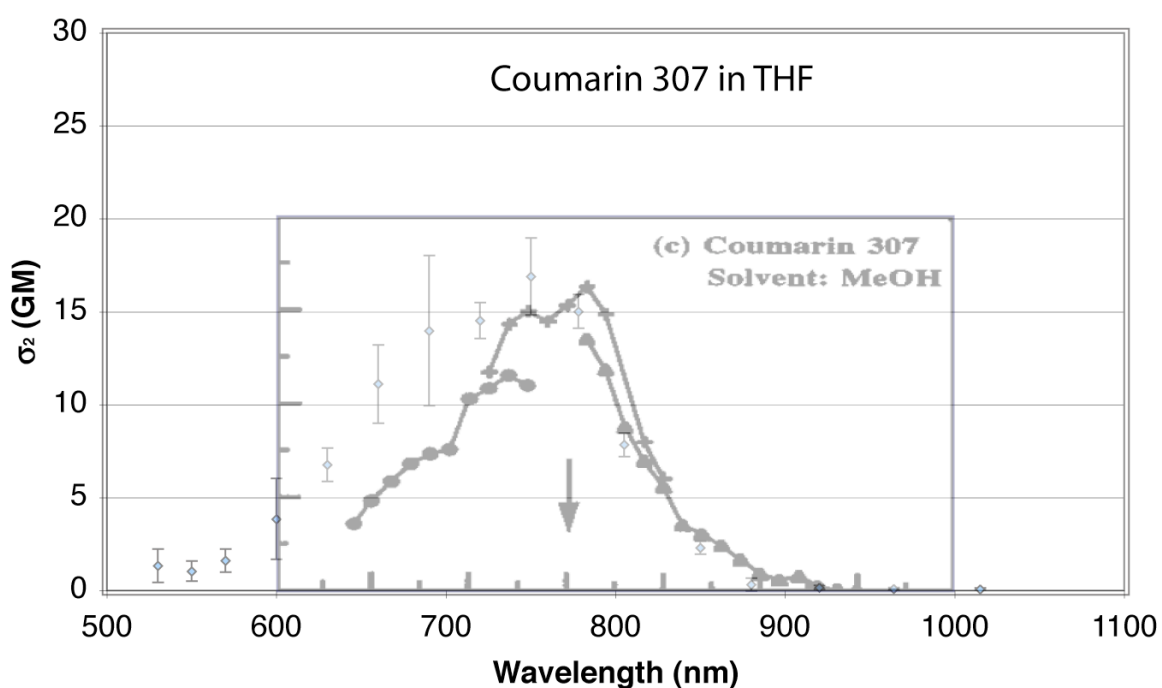


Figure 13 Results for Coumarine 307 overlapped with those of Xu and Webb.



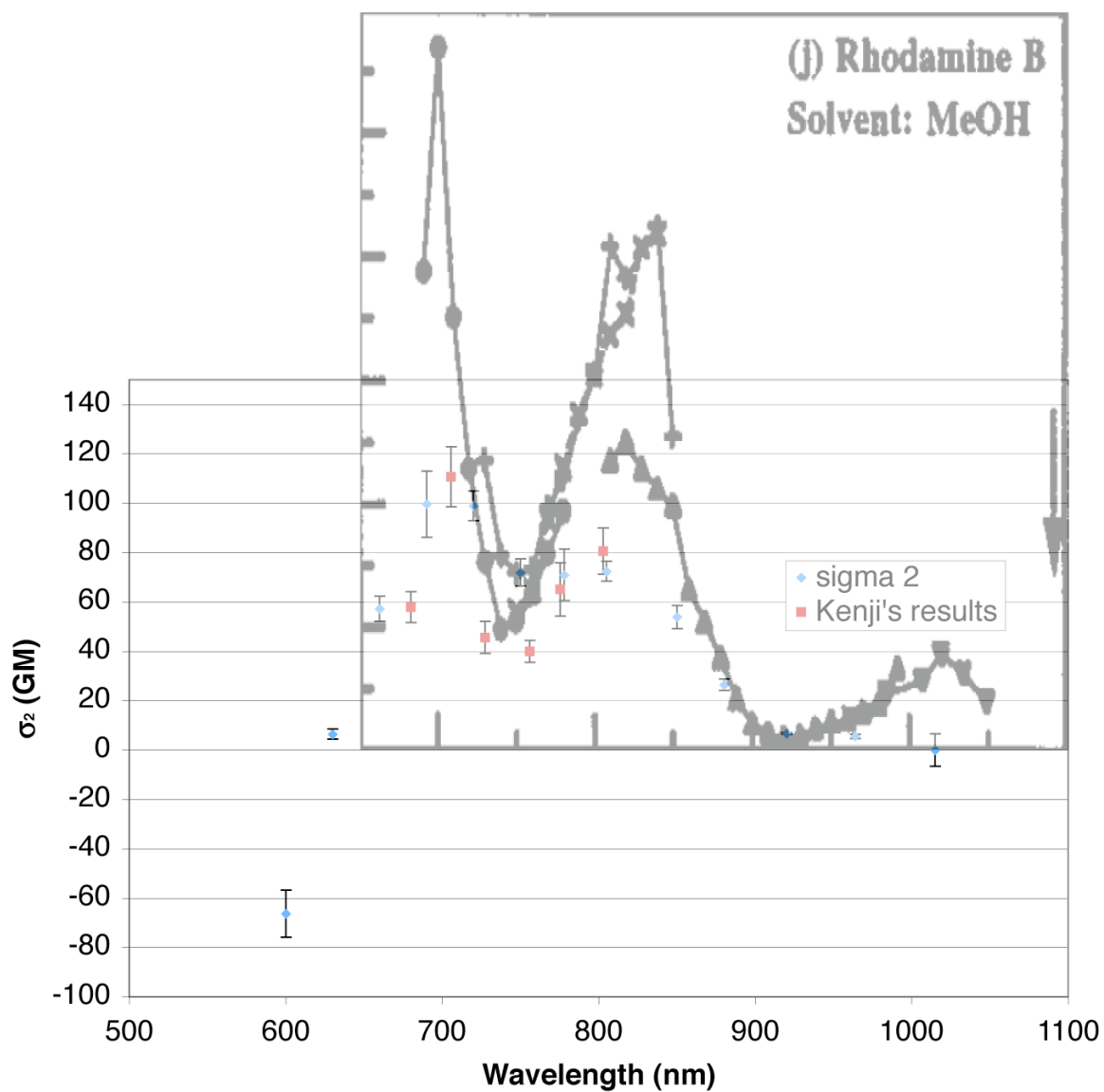


Figure 14 Results for Rhodamine B (chloride) overlapped with those of Xu and Webb.

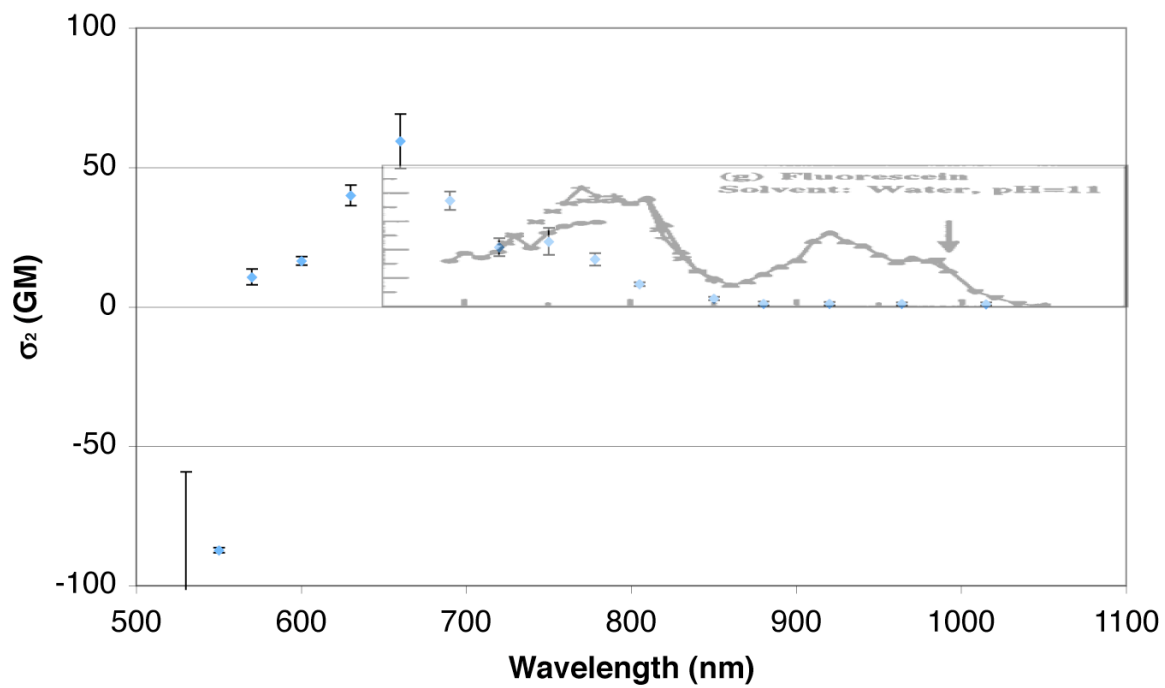


Fig. 15 Results for fluorescein overlapped with those of Xu and Webb.

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